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Port Hueneme, California 93043-4370

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THERMOCHEMICAL CONCRETE PAVEMENT SCALING MECHANISM: NAVY F/A-18 JET AIRCRAFT PARKING APRON PROBLEMS

by

Thomas Novinson, Ph.D.

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13. ABSTRACT (Maximum 200 words) Experiments were conducted to determine the mechanism of concrete "scaling" or deterioration on airfield parking aprons used by F/A-18 Navy jets. Some of the "scaling" was caused by heat from the auxiliary power unit (APU) and some was caused by phosphoric acid attack on the heated concrete. The phosphoric acid originated from hydrolysis of organic phosphates in used engine oil. The mechanism was confirmed by demonstrating that the concrete scale debris was high in phosphate content.				
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EXECUTIVE SUMMARY

This report describes the chemical analysis approach used to determine the mechanism for concrete scaling on airfield parking aprons. The Navy has observed that the concrete pavement is damaged either by aircraft chemicals or heat from the Navy F/A-18 aircraft auxiliary power unit (APU), or a combination of both.

The Acid Attack hypothesis proposes that engine oil, known to contain phosphorus compounds such as antioxidants, produces acidic compounds through oxidation and hydrolysis. The oil containing the acids drips onto the pavement and gradually decomposes the calcium carbonate or the cement paste (calcium aluminates and silicates) at the surface of the concrete. Heat from the APU accelerates this reaction and thus produces the surface scale.

This report describes the forensic chemical analysis used in determining the mechanism of the concrete scaling. Concrete debris from the airfield was extracted with hexane and the hexane was evaporated to leave an organic residue. The organic residue was analyzed by infrared spectroscopy and mass spectrometry. The extract consisted of ethanol, phenol, and other by-products expected from the decomposition of the organo phosphate compounds used as antioxidants in the engine oil. After the concrete was extracted with hexane, it was analyzed by x-ray fluorescence (XRF) and electron scanning chemical analysis (ESCA). The results indicated that the material contained calcium phosphate.

The calcium phosphate came from the decomposition of the pavement by phosphoric acid. Thus it was established that the phosphoric acid did originate from the phenyl orthophosphate and traces of red phosphorus used in the engine oil.

It is suggested that engineers mitigate the acidic erosion of the concrete either by: (a) replacing the portland cement concrete in the parking apron area with an acid resistant concrete (magnesium phosphate), or (b) recommending Military Specification (MILSPEC) engine oils without the acid-forming additives. The current acid damage to the concrete can also be lessened by periodically cleaning the affected pavement with a suitable alkaline detergent (pH 10 or higher), such as aqueous trisodium phosphate (TSP).

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INTRODUCTION

This report is part of a multi-task Navy study on thermal and chemical deterioration of concrete parking aprons used for F/A-18 aircraft maintenance. Other reports for this project have discussed: (a) thermal cycling (Refs 1 and 2) and heat stress, and (b) trapped water and steam-induced deterioration of the pavement (Ref 3) from heating of the pavement by a secondary engine on the F/A-18 known as the auxiliary power unit (APU). This report addresses the thermochemical effects of the aircraft liquids.

The aircraft fluids include: (a) a synthetic engine oil, (b) a hydraulic fluid, such as Skydrol, and (c) jet fuel, such as JP-5, which is a mixture of more than 300 aliphatic and aromatic hydrocarbons. Small amounts of these liquids drip on the pavement during aircraft maintenance operations.

The APU is a small engine, used as a generator, to provide electrical power to the jet aircraft while the main engines are warming up. The APU, located near the rear of the aircraft, is mounted so that the hot exhaust gases issue at a 45-degree angle. The heat impinges on the pavement, often in the same areas where the concrete is saturated with hydraulic fluid, engine oil, and some fuel from aircraft maintenance operations. Although these chemicals do not interact with the inert, inorganic concrete under ambient conditions, it was considered that chemical reactions could occur at elevated temperatures.

The Naval Facilities Engineering Command (NAVFAC) and its field activities have reported the formation of soft, spongy areas on the concrete parking apron where the oil and hydraulic fluid have seeped in and the pavement has been heated. The formation of this concrete "scaling" was reported earlier (Refs 1, 2, and 3) as producing foreign object debris (FOD) that poses a threat to the safety and reliability of the jet engines. The engines cost as much as \$10 million. Intake of the smallest amounts of FOD can produce hundreds of thousands of dollars of damage to the engines, not to mention the down time for the aircraft while the engines are being repaired. Thus, it is vital to solve the problems of pavement scaling. The first step in finding a solution is to determine the actual mechanism of the scaling effects. The key technical questions are: (a) what chemicals are causing the damage, and (b) can the pavement formulation or the aircraft fluid formulations (oil and hydraulic fluids) be changed to prevent this scaling problem.

ALKALINE HYDROLYSIS HYPOTHESIS

The Air Force has observed a similar type of concrete scaling on the parking aprons used to service the B-1 bombers. Wright-Patterson Laboratory at Tyndall AFB Panama City, Florida (formerly the Air Force Engineering Service Center) studied the pavement deterioration 2 years prior to the Navy.

The Air Force concluded that scaling was produced by the reaction of the esters in the synthetic engine oil with calcium hydroxide in the pavement. This Alkaline Hydrolysis reaction is shown below in Equation 1:

Eqn 1 Alkaline (Concrete) Hydrolysis of Engine Oil



alkali (A) ester (B) calcium salt (C) alcohol or phenol (D)

Notes:

A= calcium hydroxide is an alkali remaining in the concrete

B= alkyl and aromatic esters present in the MILSPEC engine oil

C= calcium salt of the carboxylic acid from the alkyl or aromatic ester

D= alcohol (ROH) is produced when the ester is aliphatic, i.e., R = methyl, ethyl, or propyl

phenol (ROH) is produced when the ester is aromatic, i.e., R = phenyl, cresyl, or xylyl

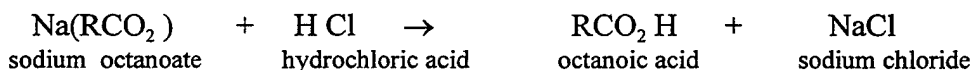
The Air Force reported (Ref 4) that a soft, soapy material was isolated that had the rancid odor of calcium hexanoate and calcium octanoate.

The Air Force investigators performed a series of chemical reactions on the concrete scaling debris to convert it into hexanoic and octanoic acids, as shown below:

Eqn 2 Conversion of Calcium Salt to Sodium Salt (For Chemical Analysis)



Eqn 3 Decomposition of Sodium Salt into Octanoic Acid (For Chemical Analysis)



The infrared spectrum (IR) and mass spectrum (MS) of the octanoic acid was prepared as proof of the reaction mechanism. The chemical schematic does not prove that alkaline hydrolysis of the esters was the prime mechanism for the concrete scaling:

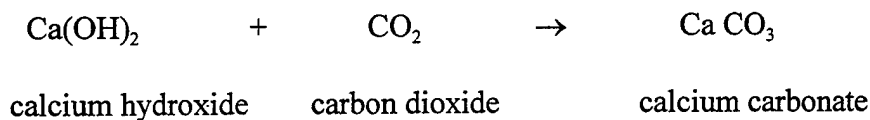
1. The concrete debris might only have contained the oily esters, or partially decomposed esters (converted into the weak hexanoic and octanoic acids) without attacking the concrete pavement.

2. The isolation and identification of hexanoic and octanoic acids does not prove that the calcium hexanoate and octanoate were formed on the surface of the pavement. The isolation of these carboxylic acids could have resulted from: (a) hydrochloric acid hydrolysis of unreacted

ester, or (b) bacterial degradation of the hexanoate and octanoate esters into the corresponding carboxylic acids.

3. The traces of calcium hydroxide known to be in the pavement are quickly converted into calcium carbonate at the surface (Refs 5 through 8). Calcium hydroxide in freshly cast concrete absorbs and reacts with carbon dioxide from the air during the 28-day curing time. The calcium carbonate layer is often as thick as 0.25 inch.

Eqn 4 Carbonation of Concrete (Cement Paste)



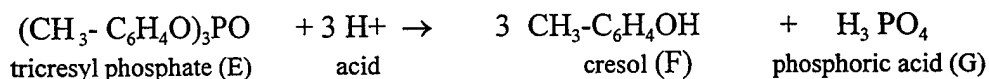
The Navy proposed another explanation for the decomposition and scaling of the concrete surface in the presence of chemicals and heat. The hypothesis is discussed below.

ACID ATTACK HYPOTHESIS

Phosphoric acid can be formed in engine oils containing alkyl or aryl phosphates. The Army provided the Naval Facilities Engineering Service Center (NFESC) with the specifications for MIL-L-23699 engine oil. This oil was known to contain a large number of additives. Tricresyl orthophosphate and triphenyl phosphite were among these chemicals. These compounds help lubricate steel and reduce wear due to heat and friction. A small amount of red phosphorus is also added to the engine oil to act as a scavenger for oxygen and water. Phosphorus oxidizes to phosphorus oxides that produce phosphorous and phosphoric acids. These acids actually protect steel from further corrosion by forming a thin layer of ferric phosphate on the metal.

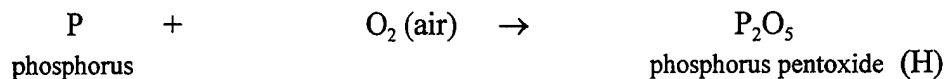
Tricresyl phosphate (E) can be decomposed into cresol (F) and phosphoric acid (G). The acid readily attacks concrete much in the same way as nitric or hydrochloric acids.

Eqn 5 Acid Hydrolysis of Phosphate Ester in Engine Oil



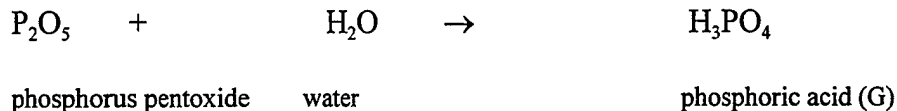
Red phosphorus is oxidized in air to form phosphorus pentoxide (H):

Eqn 6 Air Oxidation of Phosphorus in Engine Oil



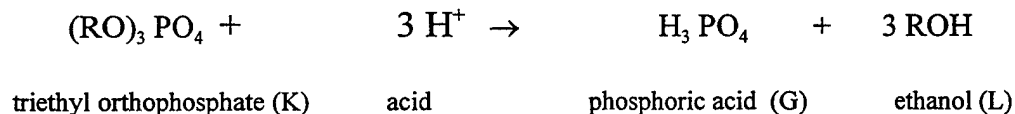
The phosphorus pentoxide reacts with water (even moisture in the air) to form phosphoric acid (G):

Eqn 7 Hydrolysis of Phosphorus Pentoxide in Engine Oil



And finally, triethyl orthophosphate (K), also used as a corrosion inhibitor, breaks down in the presence of acid, moisture, and heat to form phosphoric acid (G) and ethanol (L):

Eqn 8 Acid Hydrolysis of Alkyl Phosphates in Engine Oil



The Acid Attack hypothesis is: Triethyl orthophosphate and related chemicals in the oil are decomposed by heat, water, and air oxidation. Phosphoric acid results, and this acid attacks the concrete and produces calcium phosphate. The calcium phosphate is incorporated in the top cementitious layer of the concrete, resulting in the soft, spongy material known as “scale.”

SCIENTIFIC APPROACH

The technical approach was to: (1) collect samples of damaged and undamaged concrete from the airfield parking aprons, and (2) extract the organic materials from the damaged

concrete. The organic by-products, which would include either the intact engine oil esters (RCO_2Q) or the acids (RCO_2H) and alcohols (ROH) and phenols (QOH), could be analyzed by infrared (FTIR) spectroscopy, gas chromatography (GC), and mass spectrometry (MS). The inorganic materials, left in the concrete, should include calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$).

The R function represents alkyl groups (methyl, ethyl, propyl) and the Q function represents aromatic groups (phenyl, toluy, xylyl). Thus, ROH would represent ethanol or methanol and QOH would represent phenol or cresol.

The phosphates can be identified by x-ray fluorescence (XRF), x-ray diffraction (XRD), and electron scanning chemical analysis (ESCA), also known as photoelectron spectroscopy (PES).

In these methods, the sample is bombarded with x-rays or with photoelectrons, and the energies of the rebound particle or wave identify the elements.

The decomposition of the cement phases in the concrete is then described chemically as:

Eqn 9 a,b,c <u>Acid Decomposition of Concrete</u>				
(a)	Ca CO_3	+	$\text{H}_3 \text{PO}_4$	\rightarrow $\text{Ca}_3(\text{PO}_4)_2$ (top carbonated crust)
	calcium carbonate		phosphoric acid	calcium phosphate
(b)	CaSiO_3	+	$\text{H}_3 \text{PO}_4$	\rightarrow $\text{Ca}_3(\text{PO}_4)_2$ (cement paste)
	calcium silicate		phosphoric acid	calcium phosphate
(c)	$\text{Ca Al}_2 \text{O}_4$	+	$\text{H}_3 \text{PO}_4$	\rightarrow $\text{Ca}_3(\text{PO}_4)_2$ (cement paste)
	calcium aluminate		phosphoric acid	calcium phosphate

METHODS

The objective of this work was to track the chemical changes that took place in the oil and heat damaged concrete.

The organic (oils, fuel, hydraulic fluids) and inorganic (concrete, cement paste, aggregates) materials can be effectively analyzed and chemically identified using standard and advanced qualitative analysis described in modern chemistry text and laboratory manuals (Refs 9 through 12).

To summarize, the following chemical analytical techniques were used for the organic and inorganic analysis:

Inorganic Materials

Concrete
Aggregate
Cement

Organic Materials

Engine oils
Hydraulic fluids
Fuel

The analytical chemistry methods that were selected included:

Inorganic Analysis Methods

X-Ray Fluorescence (XRF)
Electron Scanning
Chemical Analysis (ESCA)

Organic Analysis Methods

Infrared Spectroscopy (IR)
Mass Spectroscopy (MS)
Gas Spectroscopy (GC)

The analytical methods consisted of the following:

1. Collect the crude concrete scale from the airfield apron (dirty concrete).
2. Extract the concrete with hexane to recover all organic materials. Reserve the concrete for inorganic analysis
3. Extract the same concrete samples with ethyl acetate (clean concrete). Chill the ethyl acetate extract to -10°C to see whether calcium hexanoate or octanoate was present (these salts should be soluble in hot ethyl acetate).
4. Reserve the hexane extract for chemical analysis (using IR, GC, MS). Evaporate the solvent to recover the nonvolatile products (oils or solids). Run the IR. Run the GC-MS.
5. Analyze the clean concrete sample for inorganic materials using XRF. Run ESCA on the same concrete specimen.

RESULTS

The data for the FTIR, GC, MS, and ESCA are presented in Figures 1 through 15. In Figure 1, the gas chromatogram (GC) is presented for MIL-L-23699 engine oil. The large number of peaks indicates a large number of chemicals in the engine oil, including both the esters (which make up about 70 percent of the oil) and the various antioxidant and lubricating agents.

Figure 2 shows the infrared spectrum (IR) of the fresh engine oil, taken in our laboratory. The spectrum exhibits several unique "fingerprints" in the region around 3,000 wave numbers (wn) representing the alkyl and aromatic bands, at 1,750 wn for the ester groups, and peaks in the region of about 900 to 1,500 wn representing the aromatic rings in the mixture.

The next four infrared spectra show a similar pattern of bands from the organic material extracted from the scaled sections of the parking aprons at NAS Pt. Mugu (Figure 3), NAS

Miramar (Figure 4), NAS LeMoore (Figure 5), and MCAS El Toro (Figure 6) (all in California). All of the spectra have a band at or near $1,746\text{ cm}^{-1}$, which is typical of the carbonyl ($\text{C}=\text{O}$) band of the ester. The carbonyl band for the corresponding carboxylic acid should be around $1,800\text{ cm}^{-1}$ and there should be a broad peak around $3,400\text{ cm}^{-1}$ for the hydroxyl (OH) group since this compound would have the general formula of $\text{RC}(\text{O})\text{OH}$. The importance of this finding is that the esters from the MIL-L-23699 engine oil were recovered intact without any detectable decomposition to the carboxylic acid. This contradicts the Air Force finding that the calcium hydroxide in the pavement was saponifying or causing alkaline hydrolysis of the esters in the engine oil.

The ultraviolet-visible spectrum (Figure 7) of the hexane extract shows no sign of the carboxylic acid (there are no peaks seen at 400 nanometers) that would result from alkaline hydrolysis of the esters in the motor oil.

After the concrete samples from the airfield were extracted with hexane, they were scanned under the electron microscope, which also produces XRF that identifies many elements. Figure 8 shows the XRF spectrum of pure, analytical grade calcium phosphate. The most pronounced peaks are the calcium peak at about 13.8 and 14.0 keV and the phosphorus peak at 12.0 keV.

The XRF spectra of concrete from NAS LeMoore (Figure 9), MCAS El Toro (Figure 10), and NAS Miramar (Figure 11), clearly show the presence of calcium phosphate.

The hexane soluble organic phosphates and phosphites were all extracted out of the concrete with hexane. That means that the phosphorus peak observed in the XRF spectrum is due to inorganic phosphates. Conventional concrete does not contain phosphates, so it is very likely that the phosphates came from attack of phosphoric acid, which does convert calcium salts into calcium phosphates.

DISCUSSION

If the Alkaline Hydrolysis hypothesis was correct, that is, if the alkyl hexanoate and octanoates in the engine oil were being decomposed by the alkaline hydrolysis of calcium hydroxide in the concrete, it should have been possible to obtain calcium hexanoate and octanoate from Navy airfield parking aprons. If these materials were present, the calcium hexanoate and octanoate could be identified directly using infrared (IR) spectroscopy. The crude material from the airfield would be purified in the laboratory (rather than converted to a sodium salt and decomposed by acid, as done by the Air Force) and its spectrum would be compared to that of pure materials made from calcium hydroxide and hexanoic and octanoic acids.

Additionally, if the Alkaline Hydrolysis was correct, the ethanol or cresol (phenol) from the reaction shown in Figure 1 would also be recovered (as a by-product). On the other hand, recovery of the un-decomposed alkyl hexanoate and octanoate (esters) or absence of the ethanol and phenol or cresol by-products, would suggest that alkaline hydrolysis was not the cause of the concrete scaling.

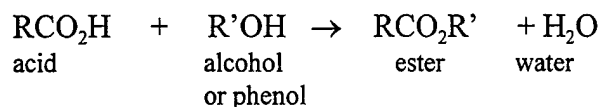
If the Acid Attack hypothesis was correct, that is, if phosphoric acid decomposition of the concrete produced the scale, we would find some calcium phosphate in the concrete, as shown in Figure 9. The calcium phosphate can be identified by: (a) x-ray fluorescence, and (b) electron scanning chemical analysis (ESCA). Both methods are needed for confirmation of the phosphate

because XRF, while quick and convenient, only indicates that phosphorus is present (not phosphate). On the other hand, ESCA is more expensive and time consuming, but it provides bond energies to confirm that phosphorus is bonded to oxygen and hence proves that phosphate is present.

It is important to know whether the concrete scale is produced by acid or alkali decomposition because the mechanism suggests how to prevent or reduce the concrete damage.

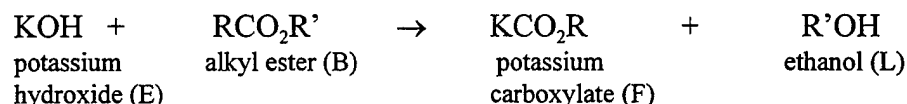
The esters that make up the engine oil were originally synthesized from the carboxylic acid and the alcohol or phenol:

Eqn 10 Synthesis of the Esters in the Engine Oil



The Alkaline Hydrolysis hypothesis (Ref 4) demonstrated that the same esters (B) could be decomposed in 4 to 6 hours by refluxing (continuous boiling and recondensation) in hot, concentrated potassium hydroxide (E):

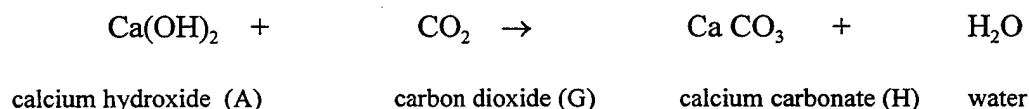
Eqn 11 Alkaline Hydrolysis of Esters with Potassium Hydroxide



The overall reaction appears to make sense at first, but there are at least four chemical mechanism problems that were not adequately addressed:

1. The calcium hydroxide in fresh concrete is rapidly carbonated by carbon dioxide (G) in the air to form calcium carbonate (H). Within a week or so, all the alkali in the top inch or so of concrete has been converted to calcium carbonate:

Eqn 12



2. The parallel between calcium hydroxide and potassium hydroxide is not very accurate. Potassium hydroxide is a much stronger alkali than calcium hydroxide and is at least 100 times more soluble in water than the latter (about 300 grams of KOH dissolve in a liter of water at 25°C; only about 2 grams of calcium hydroxide dissolve in a liter of water under the same conditions).

That means that at least 100 times as much calcium hydroxide would have to be available to saponify (decompose under alkaline conditions) the ester. This would also require a considerable amount of water under reflux conditions to accomplish the same reaction. Although the pavement would be heated by the APU, this is not the same as refluxing an aqueous mixture of alkali with the esters of the engine oil.

3. It has been shown that the calcium hydroxide is not at the surface of the concrete, where the alkaline hydrolysis took place. However, it was reported that calcium hydroxide was found further below the surface. This suggests that the esters, such as neopentyl caproate, would have to diffuse down to a level at least 1 inch below the surface to react with the alkali. However, concrete is such a good thermal insulator that even if the surface temperature was 160°C or higher (about 350°F) from the APU, the interior surface would be much lower. The direct reaction of the ester with calcium carbonate is highly unlikely from the chemistry and thermodynamics standpoint because calcium carbonate is essentially a neutral "chalk" and does not react like an alkali.

4. Finally, there are some problems with the method of isolating and identifying the calcium salt and separating the carboxylic acid. If calcium hydroxide did react with an ester, such as neopentyl caproate, one would expect the products to be calcium caproate (the calcium salt, C, in the first chemical equation) and neopentyl alcohol (D, in the same equation). It was reported that the calcium salt (C) was extracted with saline solution. Calcium salts of carboxylic acids are generally waxy, water-insoluble materials similar in chemical composition to the "bathtub scum" that forms from soap (a sodium salt of carboxylic acids) and the calcium salts in "hard water." Most people familiar with "bathtub scum" would agree that this calcium salt is virtually insoluble in tap water and even less soluble in salt solution (saline) or ocean water.

It was reported that the saline solution containing the calcium caproate salt was acidified. They extracted the free carboxylic acid (caproic) from the saline using ether. The ether was evaporated and they obtained the small amount of free carboxylic acid (such as caproic acid from neopentyl caproate). However, it could also be suggested that a few droplets of the undecomposed ester were carried along with the saline solution and were decomposed by the hydrochloric acid to accomplish the same analysis. This doesn't prove that the calcium salt ever formed.

Furthermore, there is no evidence in the concrete literature that esters attack concrete. There is evidence that many types of acids attack concrete, and some cause the same type of scaling.

CONCLUSIONS

The chemical analyses performed for this project strongly supports the Acid Attack Theory, that is, the theory that phosphoric acid causes the concrete scaling, especially when the pavement is hot. Portland cement concrete does not contain phosphates. The fact that calcium phosphate was identified by two different methods (XRF and ESCA) after the concrete scale was extracted with organic solvents, demonstrates that phosphoric acid attacked the concrete. Calcium phosphate is the final product regardless of whether the phosphoric acid reacted with the calcium carbonate (at the surface of the concrete) or the calcium aluminates, silicates, and silico ferrates (in the concrete).

In order to control the concrete scaling, it is recommended that: (1) the portland cement concrete be replaced with aluminum or magnesium phosphate concretes, which resist phosphoric acid, or (2) that the pavement be frequently washed with trisodium phosphate (or other alkaline detergent) and rinsed with water to neutralize the phosphoric acid.

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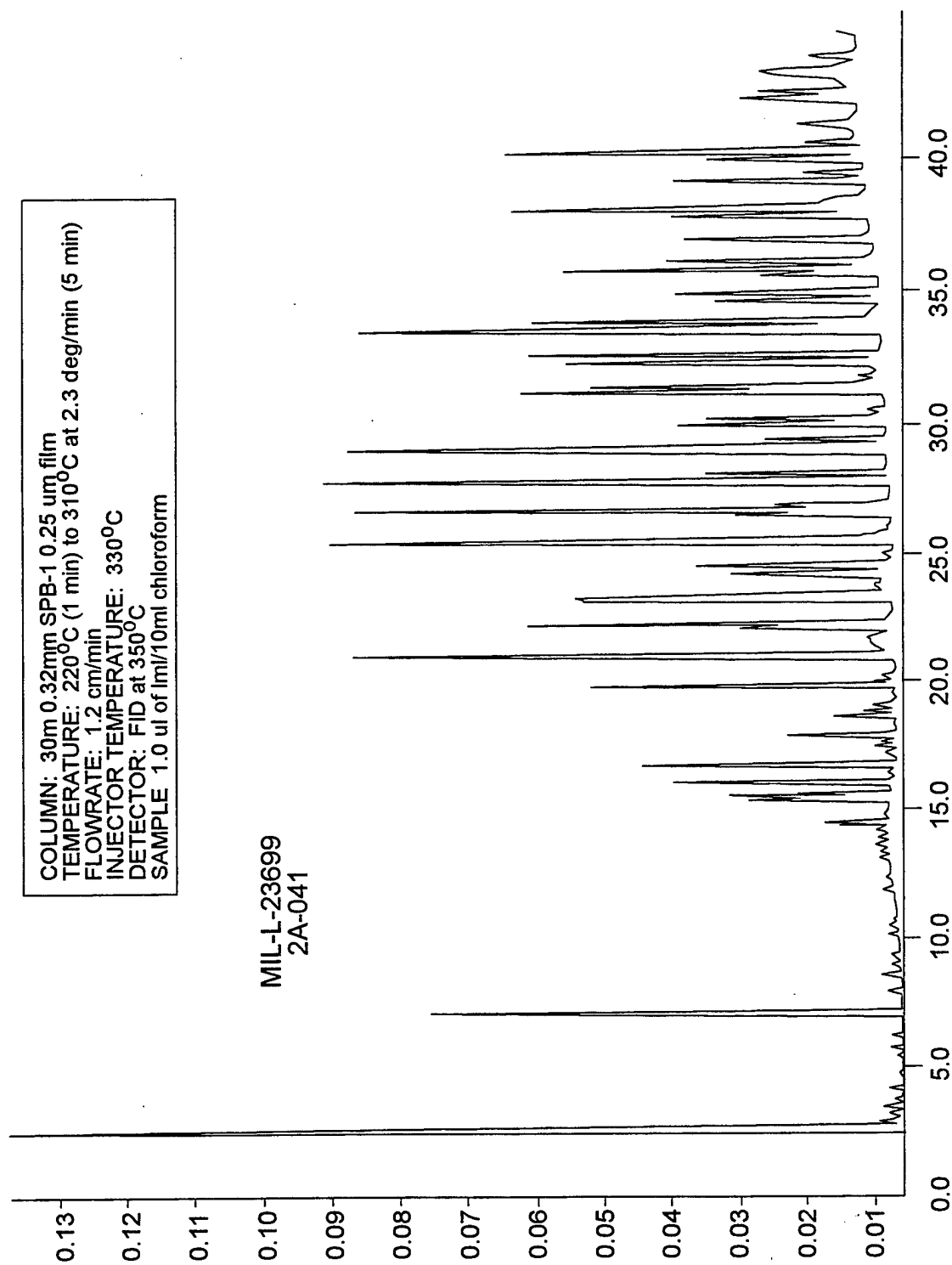


Figure 1. Gas Chromatogram (GC) of Oil MIL-L-23699.

BIO-RAD

Classic Long Chain
Ester Peaks:
-- 1745
-- 1465
-- 1375
-- 1240
-- 1160

2958.8
2925.9
2855.8

0.20
0.15
0.10
0.05
0.00

$C=O$
1745.2
the corresponding acid carbonyl
Peak would be lower, indicating
this is an ester.
1464.7
1379.6
1236.3
1159.2
1109.8
1024.6
722.8
582.6

500 Plate cutoff point

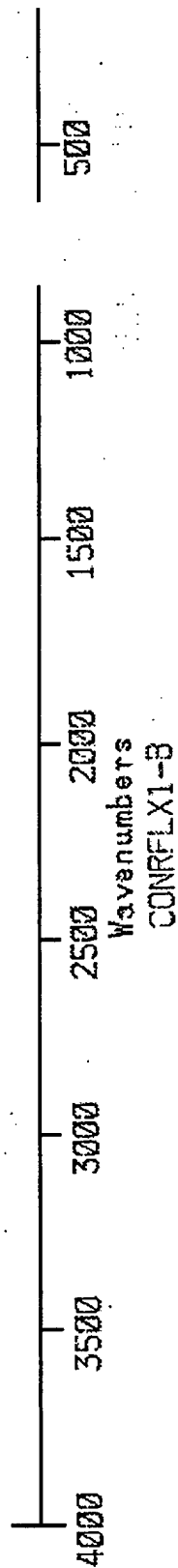


Figure 3. Infrared (IR) of Hexane Extract of Concrete Scale from NAS Pt. Mugu.

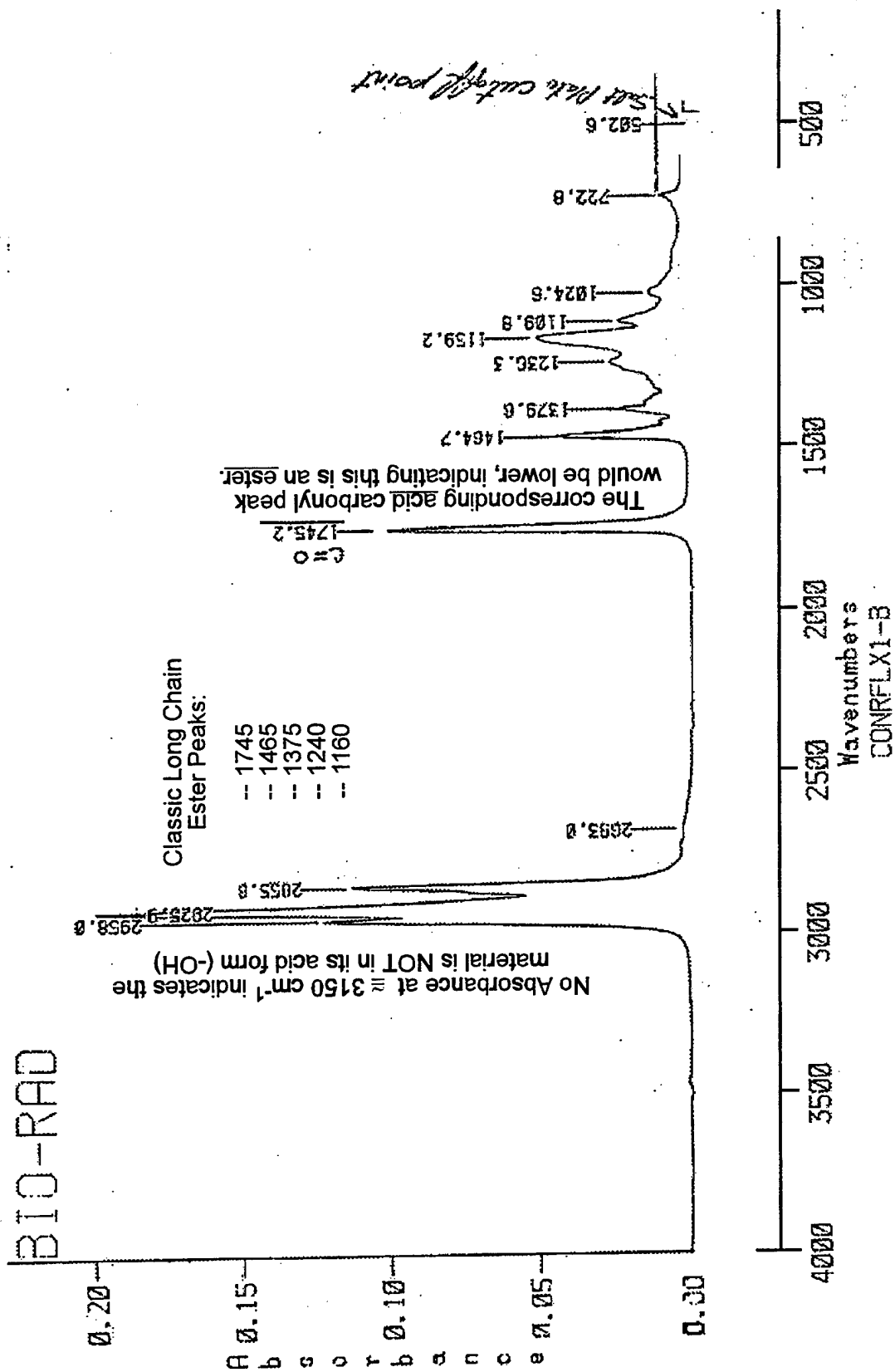


Figure 4. Infrared (IR) of Hexane Extract of Concrete Scale from NAS Miramar.

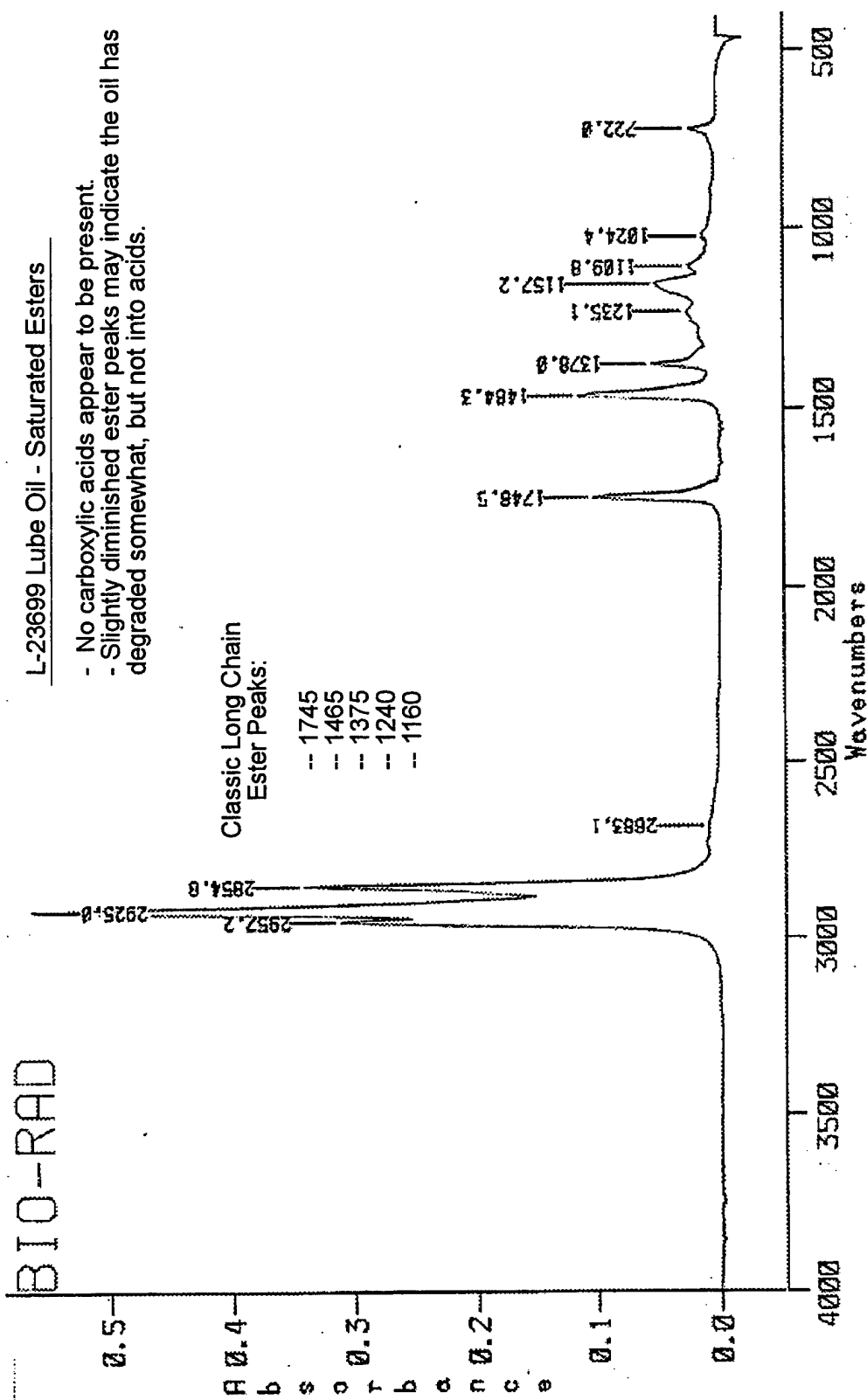


Figure 5. Infrared (IR) of Hexane Extract of Concrete Scale from NAS LeMoore.

BIO-RAD

Saturated Esters - MIL-L-23699
(no carboxylic acid appears to be present)

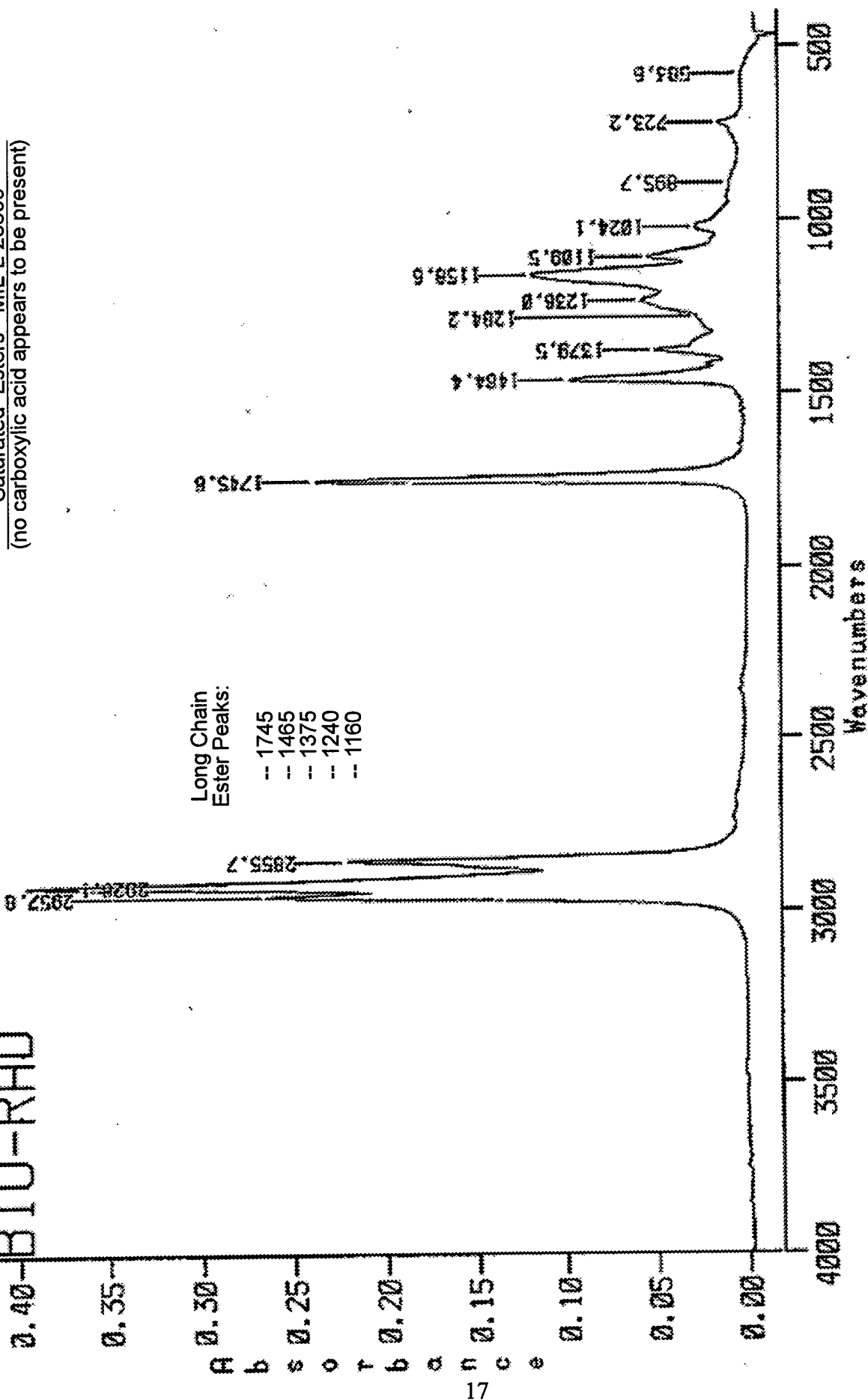


Figure 6. Infrared (IR) Extract of Concrete Scale from MCAS El Toro.

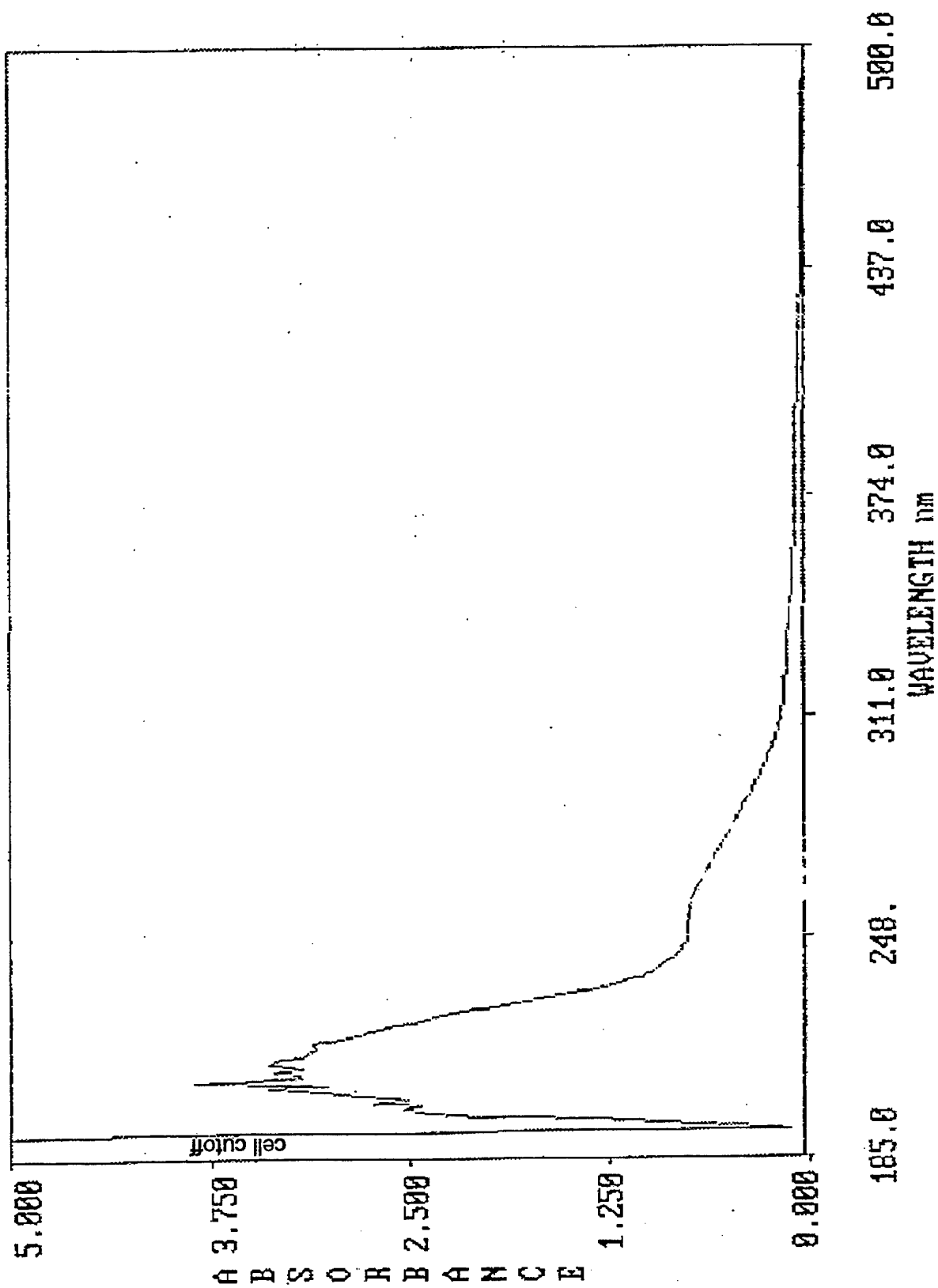


Figure 7. Ultraviolet - Visible (UV-VS) Spectrum of Hexane Extract of Concrete Scale.

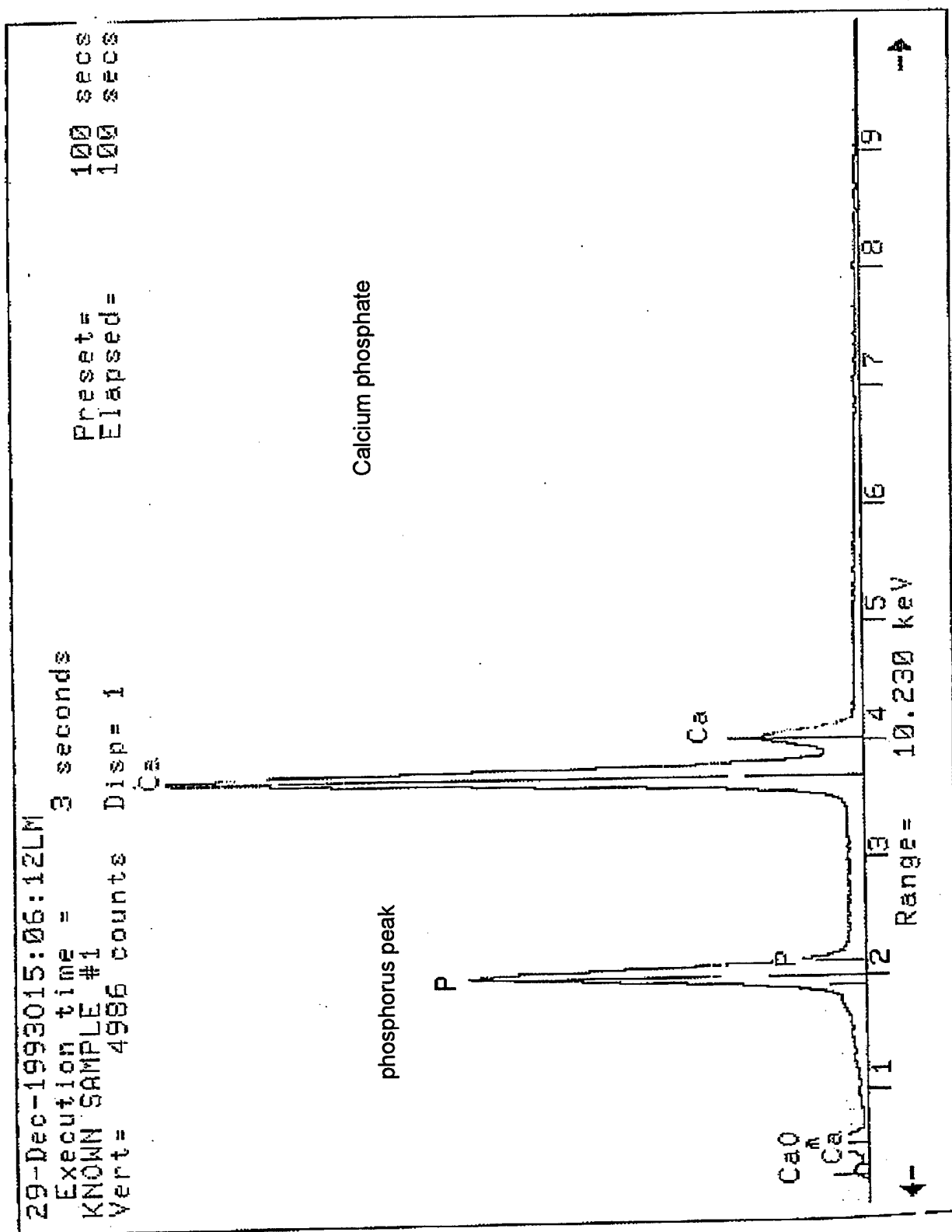


Figure 8. X-Ray Fluorescence (XRF) of Pure Calcium Phosphate.

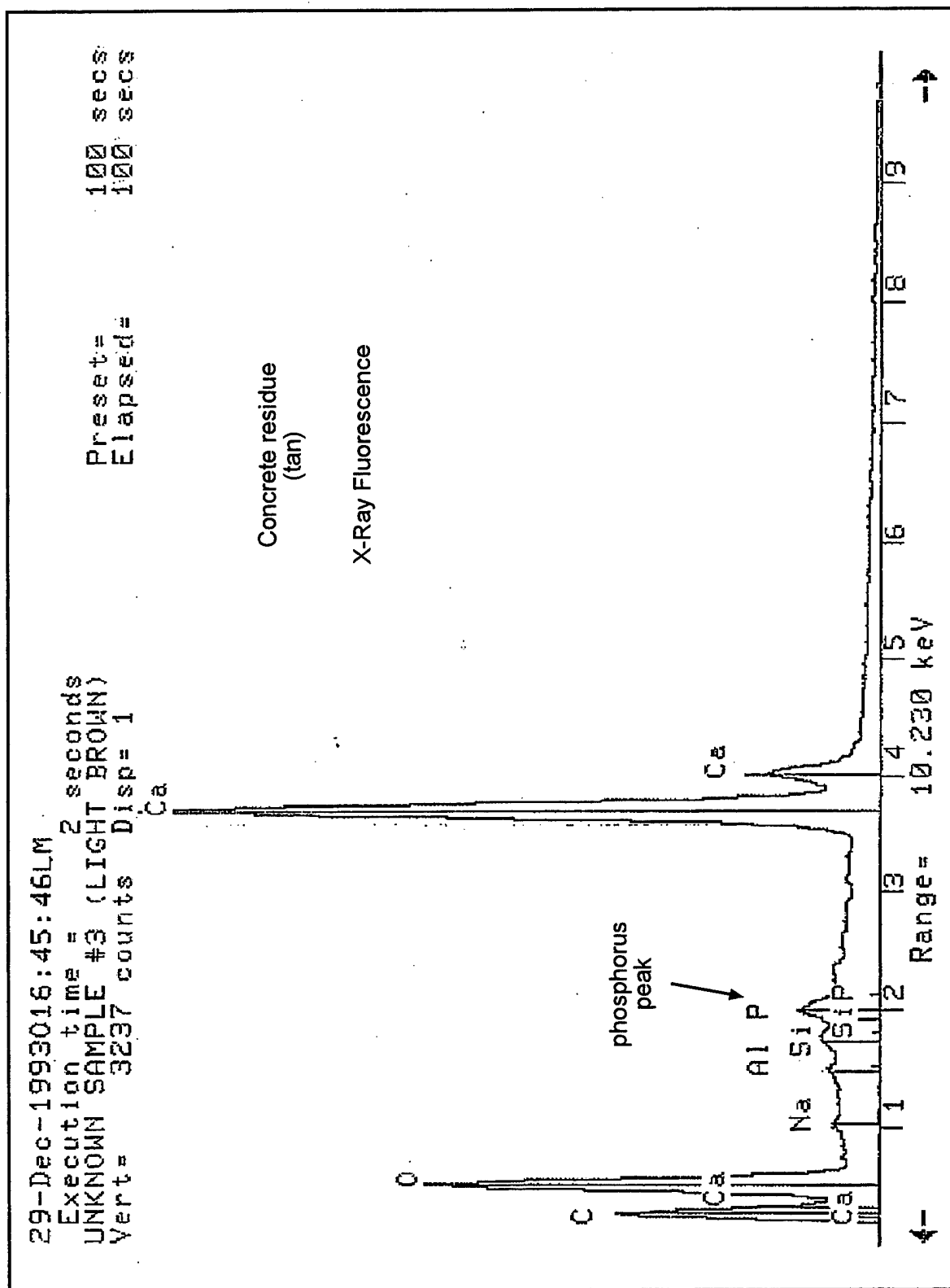


Figure 9. X-Ray Fluorescence (XRF) of Concrete Scale
 Sample from NAS LeMoore.

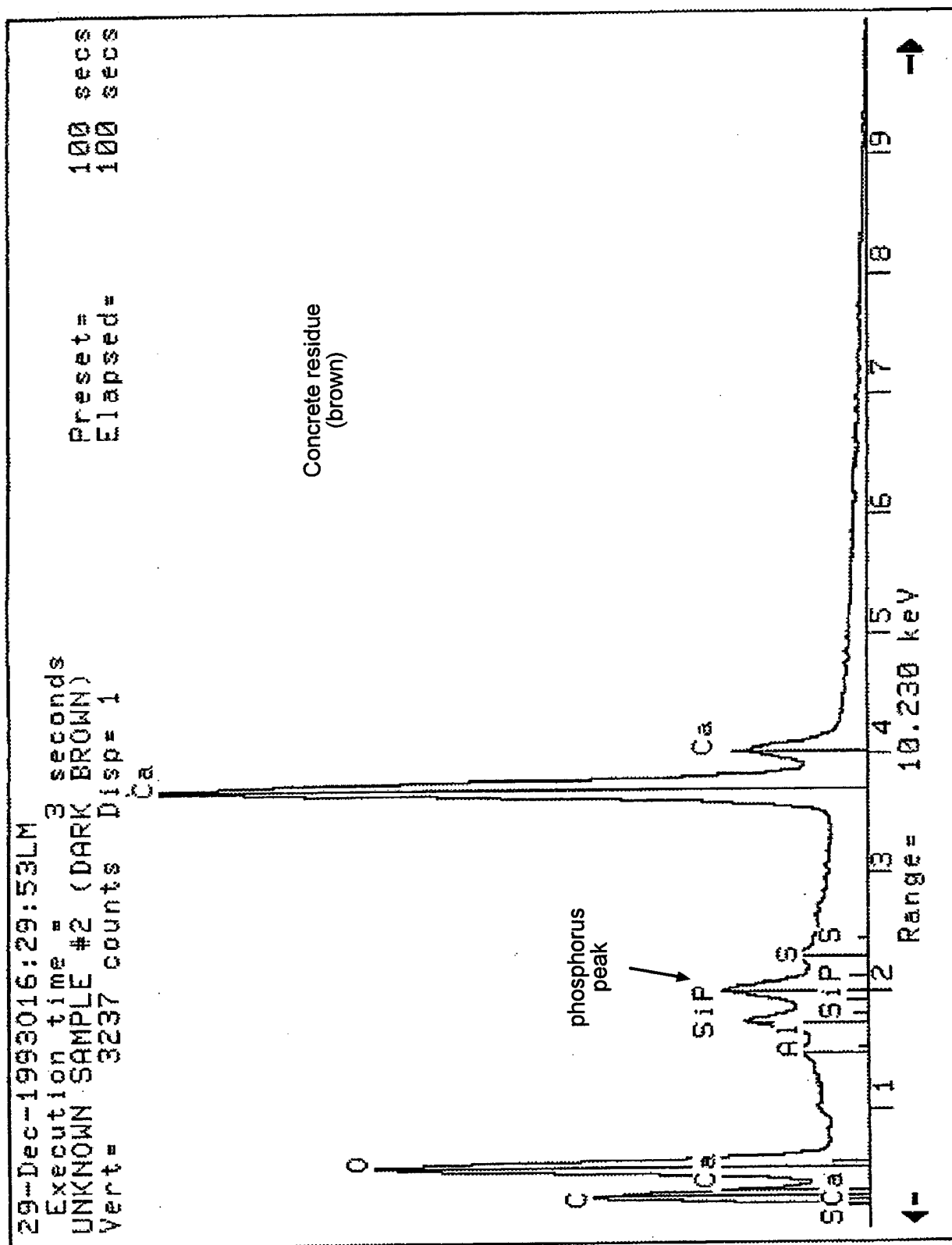


Figure 10. X-Ray Fluorescence (XRF) of Concrete Scale
 Sample from MCAS El Toro.

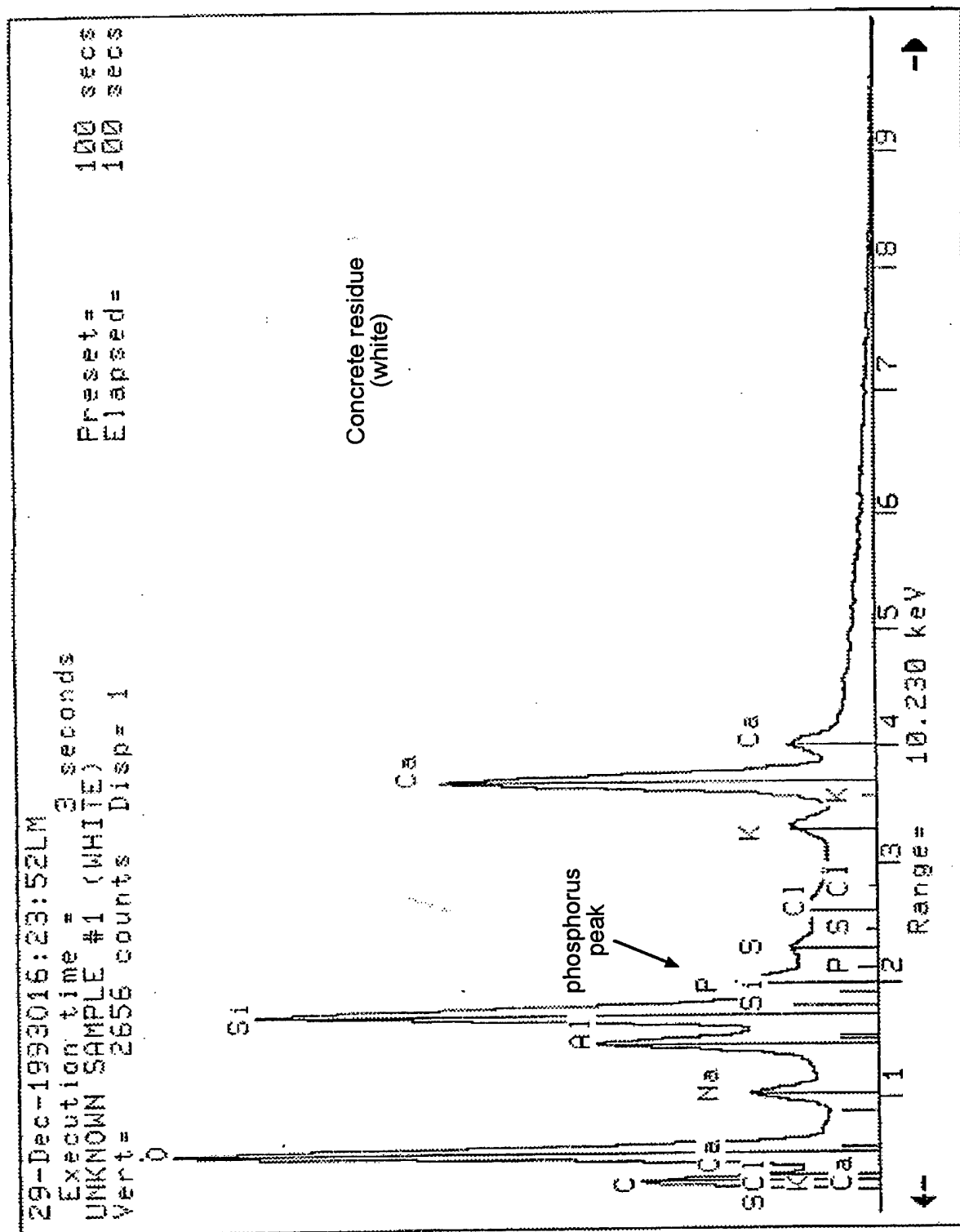


Figure 11. X-Ray Fluorescence (XRF) of Concrete Scale
Sample from NAS Miramar.

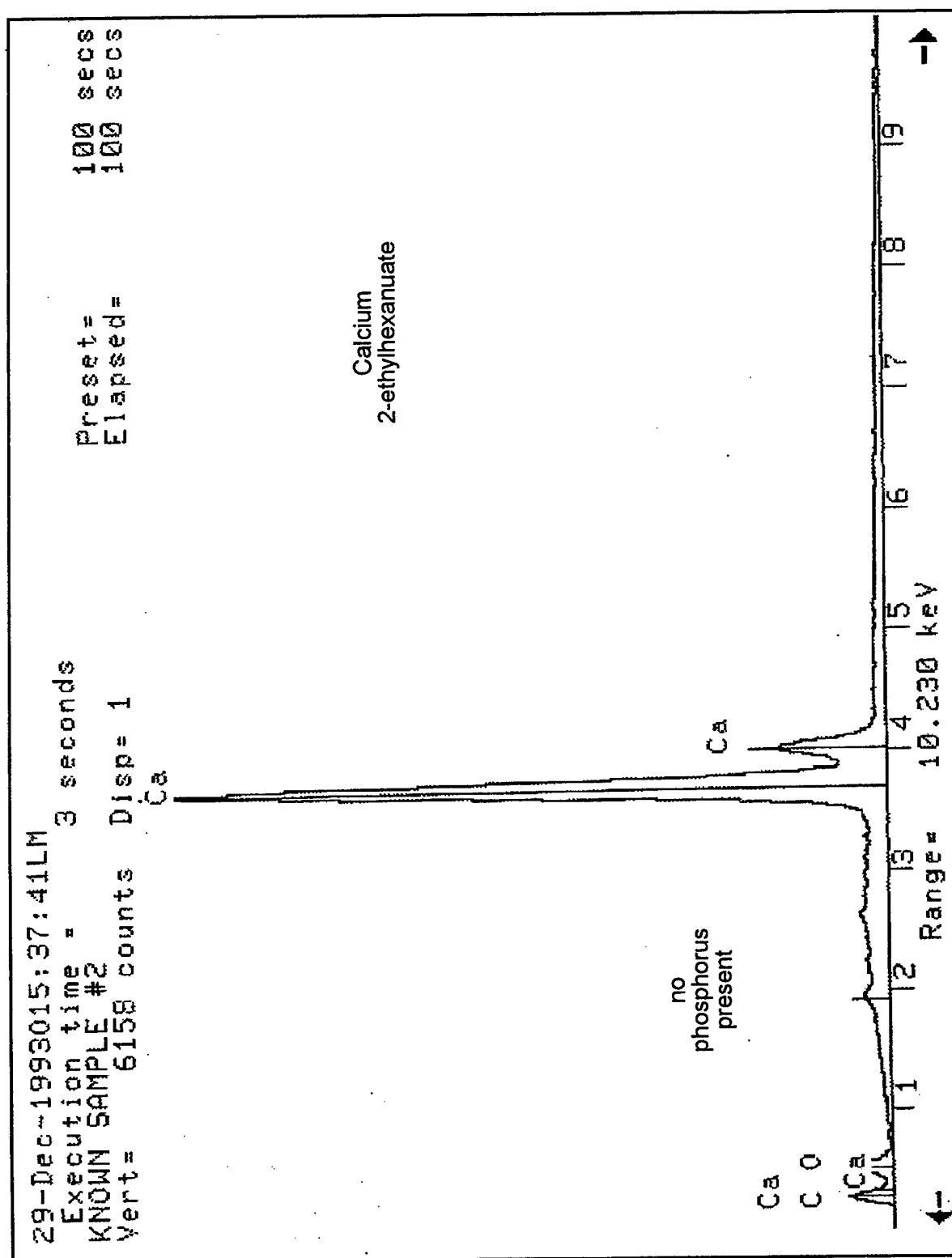


Figure 12. X-Ray Fluorescence (XRF) of the Calcium Salt of an Ester.

Resolution: 2

Spot: 500 u

Operator: AC6

Flood Gun: 7.0

X-Ray Power:

VERTICAL SCALE

1000

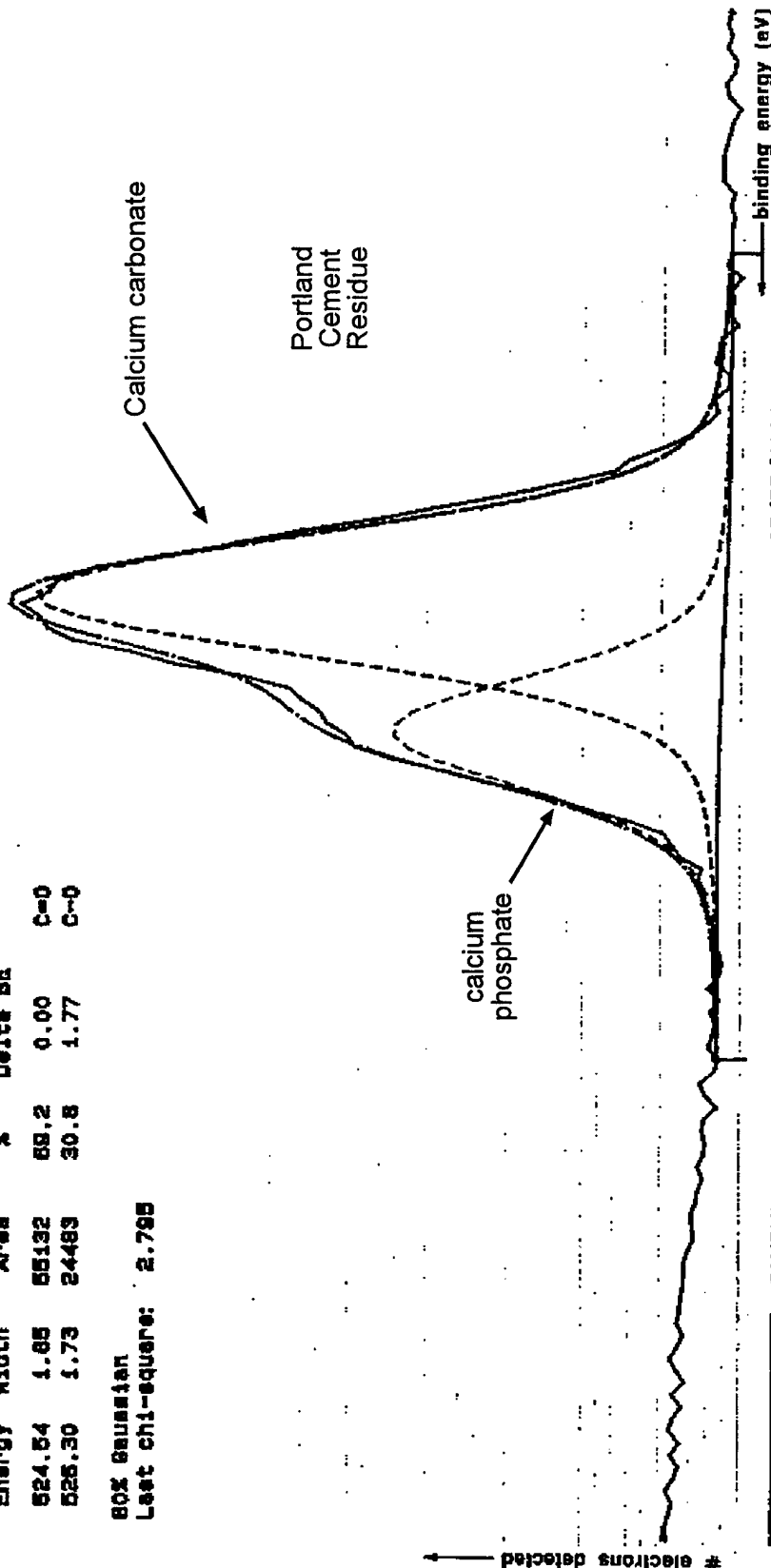
COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

Energy	Width	Area	X	Delta BE
524.54	1.85	55132	59.2	0.00
526.30	1.73	24483	30.8	1.77

80% Gaussian
Least chi-square: 2.795



537.0
UPPER BINDING ENERGY (eV)

517.0
LOWER BINDING ENERGY (eV)

SAMPLE: DATE: 12/28/1993

COMMENTS: D16C: A583 DATA FILE #A01045AA

PORTLAND CEMENT (resd) Region 2

10 SCANS
CALIFORNIA

Report #1045-1293
Spectrum #: EIC
SURFACE SCIENCE LABORATORIES 1206 Charleston Rd Mountain View California 94043 (415) 862-8767



Figure 13. ESCA Spectrum of Concrete Scale.

X-Ray Power: _____ Flood Gun: 7.0 Operator: ACS Spot: 600 u Resolution: 2

VERTICAL SCALE

2000

COUNTS/INCH

ESCA SPECTRUM

CURSOR BINDING ENERGY

Energy	Width	Area	%	Delta BE
277.61	1.44	91212	78.1	0.00
279.03	1.69	14924	12.5	1.43
281.88	1.48	13704	11.4	4.06

80% Gaussian

Last chi-square: 2.071

Calcium carbonate

Portland
Cement
Residue

calcium
phosphate

binding energy (eV)

271.0

LOWER BINDING ENERGY (eV)

SAMPLE: DATE 12/28/1993

COMMENTS: DATA FILE #A81045AA

Disc: A583

Region 1

PORTLAND CEMENT (red)

291.0

UPPER BINDING ENERGY (eV)

10 # SCANS

CALIFORNIA
SSL#8000-0034

Report #1045-1293

Spectrum #: E1B

SURFACE SCIENCE LABORATORIES 1208 Charleston Rd Mountain View California 94043 (415) 962-8767

Figure 14. ESCA Spectrum of Concrete Scale.

X-Ray Power: _____ Flood Gun: 7.0 Operator: ACB Resolution: 2

Spot: 600 u

Operator: ACB

VERTICAL SCALE

4000

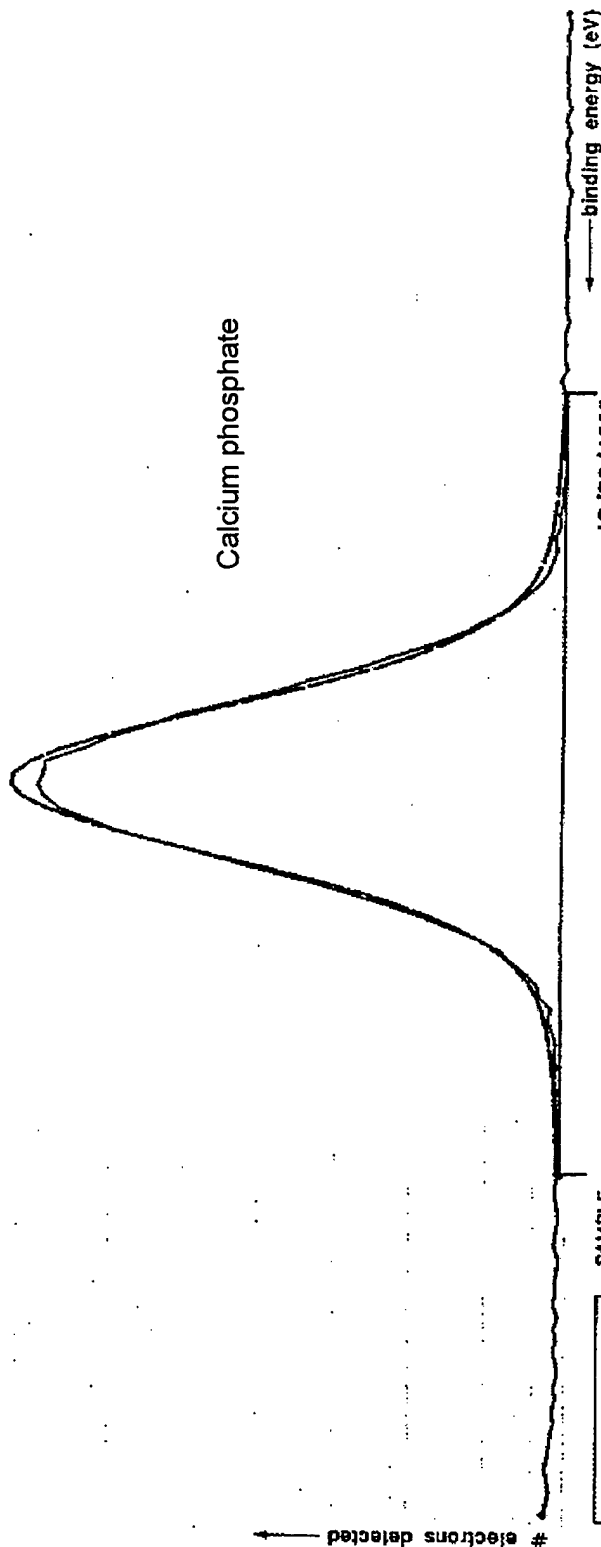
ESCA SPECTRUM

COUNTS-INCH

CURSOR BINDING ENERGY

Energy	Width	Area	%
127.11	2.39	235377	100.0
			0.00

BOX Gaussian
Last chi-square: 5.088



137.0	UPPER BINDING ENERGY (eV)	SAMPLE: DATE: 12/28/1993	117.0	LOWER BINDING ENERGY (eV)
		COMMENTS: DISC: A583 DATA FILE #A810458A		
		CALCIUM PHOSPHATE, TRIBASIC	Region 3	
50 # SCANS		Report #1045-1293		
CALIFORNIA		SURFACE SCIENCE LABORATORIES 1206 Charleston Rd. Mountain View California 94043 (415) 962-8767	Spectrum #: F2A	
ESL-7000-2004				



Figure 15. ESCA Spectrum of Calcium Phosphate.

APPENDIX A

DESCRIPTION OF INSTRUMENTAL ANALYTICAL METHODS

X-RAY FLUORESCENCE

The x-ray fluorescence (XRF) spectra were determined by Construction Technology Laboratories (CTL), a division of the Portland Cement Association (PCA) in Skokie, Illinois. The method involves scanning the sample with electrons in a vacuum, which causes x-rays to eject. The x-ray energies are analyzed and compared with known standards to identify the elements present.

The sample (concrete in this case) was coated with graphite or a thin layer of gold to make it electrically conductive. The sample was placed in a vacuum chamber and the air was withdrawn. The object was scanned with electrons from an electron gun. The sample is viewed indirectly, as a magnified image, because the electrons can be focused and bent by magnetic coils, the same as light is focused and bent through optical lenses to produce a microscope image.

The x-ray energies were detected and analyzed by the electronics, and the data on each element was printed out. The data was also displayed on the video monitor as a series of peaks representing each element.

The x-ray peak data was also printed out to record the elemental composition of the sample. There are some limitations with the XRF method. Larger elements, such as phosphorus, sulfur, chlorine, and nitrogen, are easily identified. Smaller elements, such as lithium and boron, are harder to detect. The XRF method is also limited to the larger elements in an anion. Thus, sulfur could be detected in sulfate and phosphorus could be detected in phosphates, but the oxygen was not detectable.

ELECTRON SCANNING CHEMICAL ANALYSIS (ESCA)

Electron scanning chemical analysis (ESCA) was performed by Surface Science Laboratories of Mountain View, California. This method, also known as x-ray photoelectron spectroscopy (XPS), complements the XRF/SEM method described above by identifying the energies of the chemical bonds present between the atoms. This allows the chemist or physicist the ability to identify the ions or ion clusters present, such as the silicates (Si-O-Si bonds), sulfates (S-O and S=O bonds), and phosphates (O-P=O). Thus, both the XRF and ESCA/XPS methods are needed to fully analyze the inorganic materials that make up the concrete.

INFRARED SPECTROSCOPY (IR)

Infrared spectroscopy (IR) is more useful for organic compounds, since the bending, vibration, and rotational energies of carbon bonded to other elements (C-O, C-H, C-N, and

others) are low energy transitions rather than high energy electron vibrations typical in the two x-ray and electron spectral methods described above. The absorption of IR energy by each functional group (such as a C=O in an ester or a C≡N in a cyanide) is quite characteristic of the bonding and structure of most lower molecular weight organic compounds, such as alcohols, ethers, esters, and amides. Plastics, adhesives, and the resins in coatings can also be analyzed since they are organic compounds.

The IR spectra were obtained at the Naval Facilities Engineering Service Center (NFESC) laboratory using a Fourier Transform spectrophotometer (FTIR). Earlier, it was mentioned that the concrete samples from the airfield were extracted with hexane. The hexane solutions were evaporated (generally one or two drops of the extract) onto sodium chloride (NaCl) tablets and analyzed via FTIR. NaCl is used because it is "transparent" to infrared through much of the region where organic compounds have absorbance spectra. The peaks of organic compounds occur between 2 microns to about 50 microns (most FTIR measurements are made from 3 to 20 microns).

The FTIR peaks are also designated in "wave numbers" or "reciprocal centimeters" (cm^{-1}). These units are obtained by dividing 10,000 by the value in microns. Thus, the comparison of peaks in microns and wave numbers would be :

<u>Microns (μ)</u>	<u>Wave Numbers (cm^{-1})</u>
3.0	3,333
4.0	2,500
5.0	2,000
6.0	1,666
7.0	1,428
8.0	1,250
9.0	1,111
10.0	500

GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)

Gas chromatography (GC) is used to separate chemical compounds in the vapor state. Mass spectroscopy (MS) is used to identify the individual compounds as a function of mass fragment and molecular weight. The two methods are often combined for analyzing organic compounds that can be easily vaporized without decomposition.

In the GC method, complex mixtures, such as the MIL-L-23699 engine oil, are separated into individual compounds as a function of retention time on a column. The engine oil is quite complex. The bulk of the oil consists of esters of neopentyl polyol (alcohol). The esters are made by reacting the alcohols (neopentanol) with hexanoic and octanoic acids at elevated temperatures. The resulting liquids are distilled off as esters known as neopentyl hexanoates and octanoates. Several chemicals are added as antioxidants to prevent breakdown of the oil at elevated temperatures. The chief antioxidants include PANA (phenyl-1-naphthylamine) and DODPA (dioctyldiphenylamine). These are mixed alkyl-aromatic amines that oxidize preferentially before the esters. Alkylacid salts and PTZ (phenothiazine, a sulfur based aromatic

heterocycle) are also added as antioxidants. Finally, metal deactivators are added, including BTZ (benzotriazole, a nitrogen based heterocycle, sometimes listed as an "explosive") and quinizarin (also known as dihydroxyanthraquinone) and sebacic acid (1,8-octanedicarboxylic acid). All of these compounds appear as peaks in the GC spectrum. As each component is eluted, or "washed" off the GC column, it enters the mass spectrometer (MS).

Each of these vapor phase chemicals is bombarded by a stream of electrons to form charged fragments (positive and negative). The fragments are drawn to the positive or negative poles of the electromagnet. The positive fragments impinge on a detector. Each positively charged fragment produces a specific number of atomic mass units (amu), such as 12, 23, 34, 37, 67, 98, 110, and so forth, depending on the number of carbon (12), hydrogen (1), oxygen (16), nitrogen (14), sulfur (32), and other atoms in each fragment. The resultant spectrum generally has a peak for the positively charged molecule with all the atoms intact, known as the "parent peak."

The mass of the parent peak (in amu) is useful in that it represents the molecular weight of the compound being analyzed. For example, benzotriazole, on the engine oil additives described above, has an empirical formula of $C_6H_5N_3$, which has a molecular weight of 119 (six carbons = 72, five hydrogens = 5, and three nitrogens = 42, which add up to 119 amu). Thus, one would expect to see a peak at 119. A fragment might consist of three carbons (36), two hydrogens (2), and one nitrogen (14), to produce another peak at 52 amu. By examining the entire mass spectrum, an experienced chemist would determine that benzotriazole was present. Modern computer assisted mass spectrometers generally have a library of mass spectra for several thousand compounds. Thus, the spectrum of an unknown sample can easily be matched with the spectra of many known compounds of the same structure.

Thus, a complex mixture of organic compounds (such as alcohol, carboxylic acid, and ester) can be separated and analyzed by this method. Most research chemists use both GC-MS and IR to identify unknown organic compounds, since the methods are complementary.

The GC-MS data was obtained by Surface Science Laboratories of Mountain View, California. The organics that had been extracted from the concrete samples with hexane were analyzed. The data is shown as a series of peaks on a time axis. Standards of the different chemicals must also be injected into the GC and be run under the same conditions in order to verify the nature of the compounds being analyzed.